(4) By the use of thalofide cells and low-intensity mercury arcs, it has been shown that radiation of the wave-length $\lambda = 10140$ Å.U. may be strongly absorbed by luminous mercury vapour.

(5) From the absence of absorption of radiation of wave-length $\lambda = 10140$ Å.U. by non-luminous mercury vapour, it follows that the atoms of mercury in their ordinary state do not possess a resonance potential of 1·26 volts, corresponding to $\lambda = 10140$ Å.U., in addition to the well-established one of 4·9 volts, corresponding to $\lambda = 2536{\cdot}72$ Å.U.

On the Structure of the Balmer Series Lines of Hydrogen.

By J. C. McLennan, F.R.S., Professor of Physics, and P. Lowe, M.A., University of Toronto.

(Received June 29, 1921.)

[Plate 8.]

1. *Introduction.*

It is well known that the Balmer series of the hydrogen spectrum, under moderate resolution, consists of doublets. Numerous measurements have been made of the doublet separation for H_α, but only a few of that for H_β. These are as follows:—

H_α.	$\Delta\lambda$ (Å.U.)	$\Delta\nu$ (cm.$^{-1}$).
Michelson and Morley*	0·11	0·253
Ebert†	0·132	0·306
Michelson‡	0·14	0·323
Houstoun§	0·065	0·153
Fabry and Buisson‖	0·132	0·306
Meissner¶	0·124	0·288
Merton and Nicholson**	0·132	0·306
Merton††	0·145	0·34
Gehrcke and Lau‡‡	0·126	0·293

* Michelson and Morley, 'Phil. Mag.,' vol. 24, p. 46 (1887).

† Ebert, 'Wied. Ann.' (N.P.), vol. 43, p. 800 (1891).

‡ Michelson, 'Bur. Int. des Poids et Mesures,' vol. 11, p. 139 (1895).

§ Houstoun, 'Phil. Mag.,' vol. 7, p. 460 (1904).

‖ Fabry and Buisson, 'C. R.,' vol. 154, p. 1501 (1912).

¶ See Paschen, 'Ann. der Phys.,' vol. 50, p. 933 (1916).

** Merton and Nicholson, 'Roy. Soc. Proc.,' A, vol. 93, p. 28 (1917).

†† Merton, 'Roy. Soc. Proc.,' A, vol. 87, p. 307 (1920).

‡‡ Gehrcke and Lau, 'Phys. Zeit.,' vol. 21, p. 634 (1920).

H_β.	$\Delta\lambda$ (Å.U.)	$\Delta\nu$ (cm.$^{-1}$).
Michelson	0·08	0·33
Merton and Nicholson	0·033	0·14
Merton	0·093	0·39
Gehrcke and Lau	0·0695	0·294

The only determinations which appear to have been made of the doublet separation for H_γ and H_δ are those recently obtained by Gehrcke and Lau.* Their result for H_γ is $\Delta\lambda = 0{\cdot}058$ Å.U. ($\Delta\nu = 0{\cdot}307$ cm.$^{-1}$), and for H_δ is $\Delta\lambda = 0{\cdot}0432$ Å.U. ($\Delta\nu = 0{\cdot}257$ cm.$^{-1}$). The outstanding feature of the results given above, it will be seen, is the lack of agreement exhibited by the numbers for H_α and H_β.

While some spectroscopists have taken the Balmer series to be a principal one, others have considered it to be a subordinate series. From an inspection of the values recorded above, it is difficult to reach a definite conclusion respecting the type to which the Balmer series should be assigned. The general trend of the numbers representing the frequency differences is in the direction of a decrease, with the progress of the series towards the violet. This might lead one to conclude the type was that of a principal doublet series. Such a conclusion, however, is scarcely warranted, for Gehrcke and Lau, who found for the doublet separation of the first four members, $H_\alpha = 0{\cdot}29$, $H_\beta = 0{\cdot}29$, $H_\gamma = 0{\cdot}3$, $H_\delta = 0{\cdot}26$ cm.$^{-1}$—values which show a tendency gradually to decrease—have stated their results are to be taken as supporting the view that the frequency difference of the doublet components is constant for all members of the series. Departures from this law exhibited by their numbers are to be considered as coming within the limits of error of the observations.

In applying to hydrogen his theory of the fine structure of spectral lines, developed by extending Bohr's theory of the origin of radiations, and incorporating with it the principle of relativity, Sommerfeld† has shown that each member of the doublet H_α should consist of a close triplet, each member of H_β of a close quartette, each member of H_γ of a close quintette, etc. He has shown, moreover, that his theory lends itself to the precise calculation of the intensities of these constituents of the doublets. Sommerfeld has found, too, that, theoretically, the magnitude of the doublet separation should be constant for all members of the Balmer series, and equal to

* The investigation described in the present communication was begun, and measurements were made on the separation of the components of H_α, H_β, H_γ, and H_δ, before the publication of Gehrcke and Lau's paper.

† Sommerfeld, 'Ann. der Phys.,' vol. 51, p. 1 (1916); also 'Atombau und Spektrallinien,' p. 344.

0·365 cm.$^{-1}$. In the case of H_α, H_β, and H_γ, the calculated distribution and intensities of the fine structural components is such that, in actual determinations of the doublet separations, values less than 0·365 cm.$^{-1}$ should be obtained. For H_δ, and the higher members of the series, effects connected with the fine structure of the components of the doublets should be less in evidence. It follows, therefore, that in proceeding from H_α to the higher members of the Balmer series, we should expect, on the basis of Sommerfeld's theory, to obtain for the doublet separations values that rapidly increase up to 0·365 cm.$^{-1}$ for H_δ, and then remain constant for the remainder of the series.

A direct test of Sommerfeld's theory, through an examination of the structure of the doublets of the Balmer series of hydrogen, is necessarily attended with considerable difficulty. With atoms so light as those of hydrogen, the Doppler effect arising from molecular thermal agitation is considerable at ordinary temperatures. As a result, the members of the doublets cannot ordinarily be obtained as sharp lines, but as broad and more or less diffuse bands. This diffuseness is, moreover, enhanced by the Stark effect, which always exists to a greater or less extent when the emission of radiation is brought about by electrical stimulation.

What has been taken to be a remarkable confirmation of the validity of Sommerfeld's theory has been obtained by Paschen,* through a study of the structure of spectral lines belonging to series originating in the helium univalent ion. With this element the Doppler effect is less marked than with hydrogen, and, as the nuclear electric charge for helium atoms is twice as great as that for atoms of hydrogen, the lines of the spectrum of helium are less influenced than those of hydrogen by the Stark effect, and on that account are sharper.

In summing up the results of Paschen's observations, Sommerfeld has reached the conclusion that qualitatively and quantitatively, they constitute a definite and strong confirmation of his theory. A further confirmation is found in the fact that the L. series of the Röntgen spectra of the elements consists of doublets with a constant separation between the components of approximately 0·365 cm.$^{-1}$.

In discussing Sommerfeld's theory and its supposed confirmation by Paschen, Stark† has pointed out that a vital characteristic of the theory lies in its quantitative features. He has drawn attention in particular to Paschen's observations on the helium line $\lambda = 4686$ Å.U. and has emphasised the latter's failure to find three components whose presence was demanded by the

* Paschen, 'Ann. d. Phys.,' vol. 50, p. 933 (1916).

† Stark, 'Jahr. d. Radioakt. und Elek.,' vol. 7, Heft 2, No. 66, p. 170 (1920).

theory, and to his observation of a component whose presence was not predicted by it. Stark also makes a point of the fact that the observed relative intensities of the components of $\lambda = 4686$ Å.U. do not agree with the values calculated by Sommerfeld. Moreover, he lays particular stress on the fact that while Sommerfeld's theory indicates that the doublet separations in the Balmer series of the hydrogen spectrum should gradually increase in passing from H_α to H_δ, the results of Gehrcke and Lau, taken as they stand, show doublet separations gradually decreasing in magnitude as we pass from the first to the fourth member of the series.

From the above it will be seen that while strong confirmation of Sommerfeld's theory has been obtained from Paschen's investigation of the structure of a number of wave-lengths in the spectrum of helium, and from an important characteristic of the L. series in the Röntgen spectra of the elements, it is highly desirable to have the validity of the theory tested directly by making accurate determinations of the doublet separations of as many as possible of the members of the Balmer series of hydrogen.

The following paper aims at giving an account of an investigation initiated with this object in view. It will suffice to state here, that in our determinations of the doublet separations of H_α, H_β, H_γ, and H_δ, values were obtained which regularly decreased from 0·36 cm.$^{-1}$ to 0·29 cm.$^{-1}$ in passing from the first to the fourth member of the series.

2. *Apparatus.*

In this investigation the doublet separations were measured with a Lummer plate, for which the optical data were the following:—

Optical Data of Lummer Plate.

	Refractive Indices. λ (Å.U.).	μ.
$l = 13$ cm.	6563·045	1·50746
$d = 0{\cdot}448$ cm.	5896·155 }	1·50990
$d\mu/d\lambda$ for $H_\alpha = -\ 324$ cm.$^{-1}$	5890·186 }	
$H_\beta = -\ 716$ „	4861·49	1·51560
$H_\gamma = -\ 960$ „	4308·08	1·52025
$H_\delta = -1150$ „		
$\Delta\lambda_m$ for $H_\alpha = 0{\cdot}4159$ Å.U.		
$H_\beta = 0{\cdot}2224$ „		
$H_\gamma = 0{\cdot}1755$ „		
$H_\delta = 0{\cdot}1550$ „		

The discharge tube made of pyrex glass, was similar in type to that used by Prof. R. W. Wood* in photographing the higher members of the Balmer series. As fig. 1 shows, its central portion was surrounded by a glass

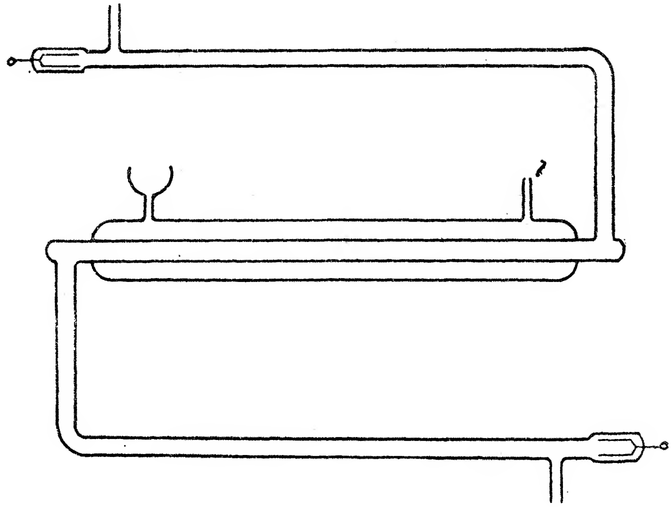


FIG. 1.

envelope that could be filled with liquid air when desired. This central portion was about 50 cm. in length, and 5 mm. in diameter. To obtain the spectrum a Hilger constant deviation spectrograph was used that was provided with a symmetrically opening slit at the entrance to the collimator tube, and with a second one at the exit of the observation tube. The light used was that which issued axially from the central position of the discharge tube. In taking photographs of the interference bands the Lummer plate was placed immediately behind the spectrograph in line with the axis of the observation tube, the fringes being brought to a focus in a camera provided with an achromatic lens of 30 cm. focus. The discharge tube was supplied with hydrogen generated in an ordinary voltameter by the electrolysis of dilute sulphuric acid. A $\frac{1}{4}$-kilowatt Clapp Eastham 15,000-volt transformer was used to produce the discharge and in most cases the transformer was operated with a current of about two ampères in the primary circuit.

3. *Experiments.*

In carrying out the experiments the hydrogen on issuing from the voltameter was led into the discharge tube after passing successfully through a drying tube filled with phosphorus pentoxide and a capillary tube curled into

* R. W. Wood, 'Roy. Soc. Proc.,' A, vol. 97, p. 455 (1920).

a spiral about 4 cm. in diameter and 8 cm. in length. A Gaede rotary mercury pump was attached to the exit of the discharge tube and was kept continuously in operation while exposures were made. In assembling the apparatus a series of trials was made with capillary tubes of different bores and lengths, until one was found, which under the continuous operation of the Gaede pump allowed the hydrogen to flow into the discharge tube at a rate which kept the pressure in the latter constant, and at the value at which it was found the transformer would give the strongest illumination.

With the symmetrically opening slits mounted on the collimator and observation tubes of the constant deviation spectrograph, no difficulties were experienced in isolating the wave-lengths H_α, H_β, H_γ, H_δ. Repeated attempts were made with the same arrangement to isolate the higher members of the Balmer series, but they were not successful. The investigation was therefore limited to the determination of the doublet separations of the first four members of the series.

When the procedure outlined above was followed, it was found out that all four wave-lengths came out quite distinctly as doublets.

When, however, the discharge tube was kept surrounded with liquid air during the exposures, all four of the wave-lengths came out on the plate as triplets. At first it was thought that this pointed to a change produced in the structure of the lines of the Balmer series brought about by the use of liquid air. It was noted, however, on measuring up the plates that the separation of two members of each triplet was the same as the doublet separations found respectively for H_α, H_β, H_γ, H_δ, when operating at room temperatures. This suggested the possibility of hydrogen being contaminated with some impurity whose spectrum became enhanced in some way when the tube was surrounded with liquid air. The spectrum of the light from the discharge was then photographed, and it was found that as soon as the envelope surrounding the discharge tube was filled with liquid air, the spectrum of nitrogen came out on the plates with strong intensity. A tube filled with cocoanut charcoal was then inserted in the gas circuit between the capillary spiral and the discharge tube, and kept cold with liquid air. When this precaution was taken the wave-lengths H_α, H_β, H_γ, and H_δ again came out as comparatively sharp and clearly defined doublets.

Reproductions of these doublets are shown in Plate 8, (1). It will be seen that all four are clearly defined.

Reproductions of the triplets for H_α, H_β, H_γ, and H_δ are shown in (2). With H_α and H_γ the third member of the triplets came out strongly, while with H_β it was comparatively weak. With H_δ the third

member of the triplet was very strong, but the pair constituting the doublet only came out faintly. In the reproduction shown in (2) the components of the doublet for H_δ are not discernible.

The different spectra obtained with the discharge tube are shown in (3). Reproduction "*a*" was obtained with the unpurified hydrogen when the discharge tube was at room temperature, and reproduction "*b*," when the discharge tube through which the unpurified hydrogen was passed, was cooled with liquid air. In this case it will be seen the spectrum of nitrogen was very strongly recorded. Reproduction "*c*" was obtained when hydrogen purified with liquid air-cooled cocoanut charcoal was passed through the tube, and the latter was kept at room temperature. Reproduction "*d*" is the spectrum of mercury. It will be seen from "*b*" that while H_β came out quite clear and at some distance from any of the wave-lengths of nitrogen which were visible, H_α, H_γ, and H_δ were recorded in close proximity to wave-lengths in the nitrogen spectrum. The triplet structure was, however, obtained with H_β, as well as with H_α, H_γ and H_δ, and this fact rather militates against the view that the third member of each of the triplets had its origin in nitrogen.

It will be seen that the secondary spectrum of hydrogen came out strongly in "*c*," and that it contained wave-lengths close to H_β, H_γ, and H_δ, but not close to H_α. It may be, therefore, that the triplet structure actually arose from a modification produced by the nitrogen in the radiation emitted by the hydrogen.

4. *Doublet and Triplet Separations.*

In determining the separation of the components of the different wave-lengths, the plates were measured up with a Hilger photo-measuring micrometer, and readings were taken with it at the edges as well as at the centres of the interference bands. The mean values of the separation of the components of the four doublets, H_α, H_β, H_γ, and H_δ, taken from centre to centre, are given in Table I. The results of Merton and of Gehrcke and Lau are also given in the Table. It will be seen that the separation gradually decreased from 0·154 Å.U. for H_α to 0·049 Å.U. for H_δ while the corresponding frequency differences dropped from 0·36 cm.^{-1} to 0·29 cm.^{-1}.

In fig. 2 the results are plotted with the wave-length differences as ordinates and the squares of the wave-lengths as abscissæ. Had the frequency difference for the components of the four wave-lengths been constant and equal to 0·365 cm.^{-1} the values of $\Delta\lambda$ would have registered more or less closely with the continuous straight line through the origin. With the results obtained by us for the separations of the doublet components, however, the

Table I.

Line.	Wave-length λ.	Separation of components.					
		Merton.		Gehrcke and Lau.		Authors.	
		$\delta\lambda$.	$\delta\nu$.	$\delta\lambda$.	$\delta\nu$.	$\delta\lambda$.	$\delta\nu$.
	Å.U.	Å.U.	cm.$^{-1}$	A.U.	cm.$^{-1}$	Å.U.	cm.$^{-1}$
Hα	6563	0·145	0·34	0·126	0·29	0·154	0·36
Hβ	4861	0·093	0·39	0·070	0·29	0·085	0·36
Hγ	4341			0·058	0·31	0·062	0·33
Hδ	4101			0·043	0·26	0·049	0·29

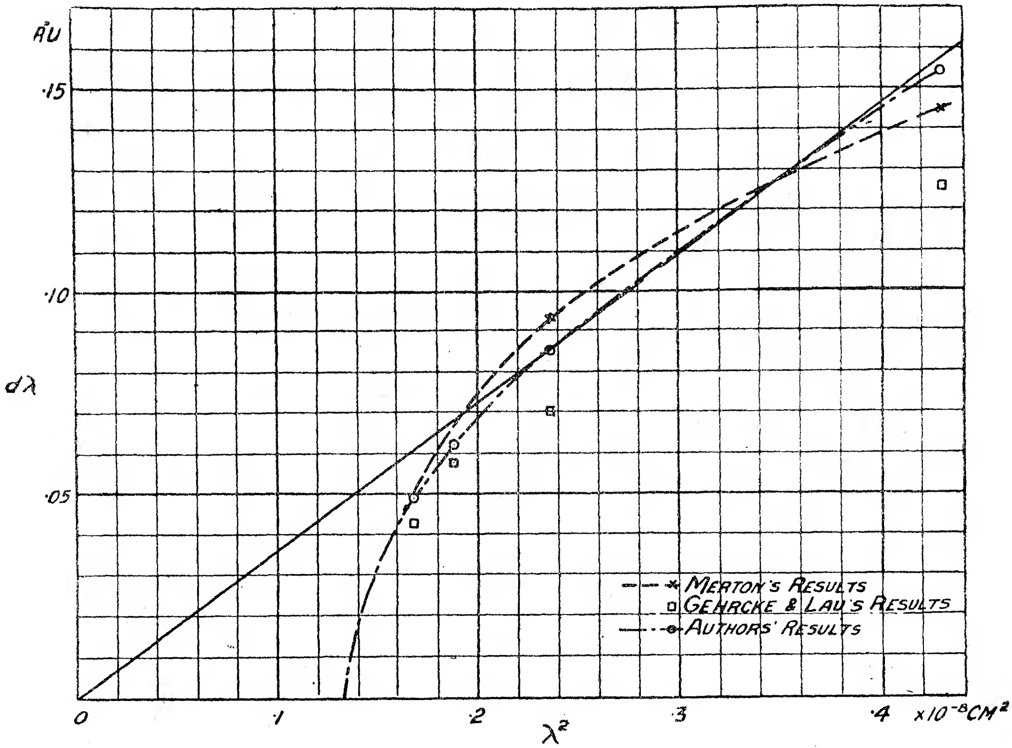
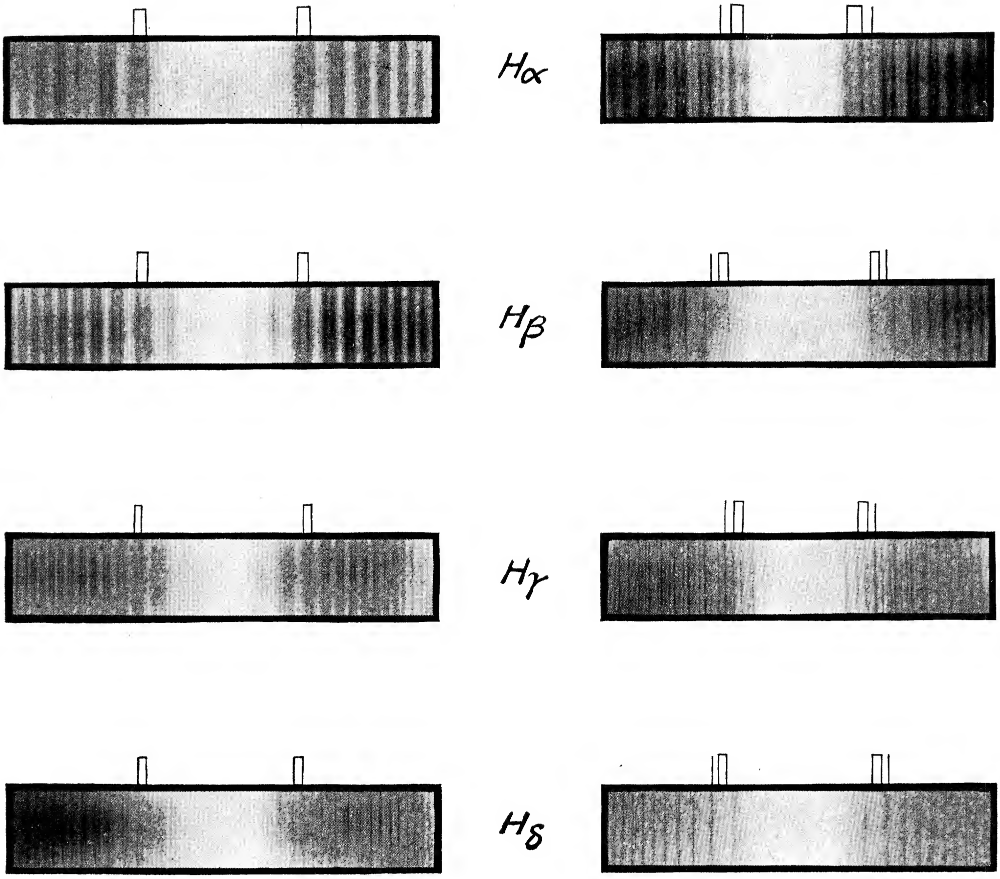
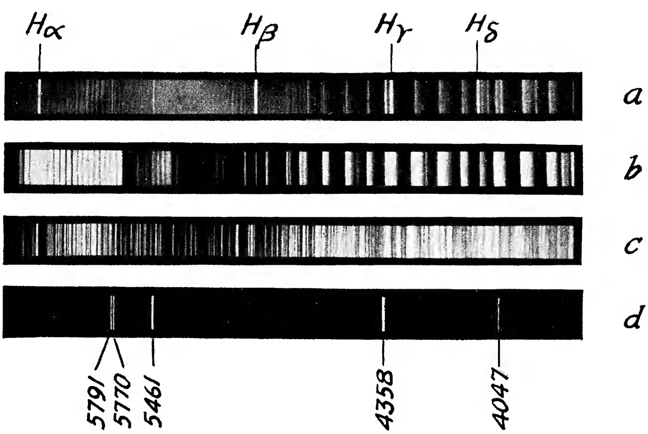


FIG. 2.

values of $\Delta\lambda$ lay close to the broken curve which when extended, it will be seen, cuts the zero ordinate line at approximately $0{\cdot}133 \times 10^{-8}$ cm.^{2}. This would seem to indicate a separation of the doublets that vanishes at $\lambda = 3648$ Å.U. the limiting wave-length of the Balmer series. Should this result turn out to be correct it would show that the Balmer series of hydrogen should be classified as a principal rather than as a subordinate series.

(1) (2)


$H\alpha$
$H\beta$
$H\gamma$
$H\delta$


$H\alpha$
$H\beta$
$H\gamma$
$H\delta$
a
b
c
d
5791
5770
5461
4358
4047

(3)

In measuring up the plates on which the triplet structures were obtained difficulty was experienced in deciding whether the third member of the triplet had a wave-length longer than the long wave-length member of the corresponding doublet or shorter than the short wave-length member of the doublet. Attempts were made to settle the point by the use of a Lummer plate crossed with an échelon grating, but the results were not sufficiently satisfactory to settle the question. With the lengths of exposure it was found possible to use, the interference points were not clearly enough recorded on the plates :—

Table II.—Separation of Triplets.

Line.	Separation of		
	1 and 2.	2 and 3.	3 and 1.
	A.U.	A.U.	A.U.
$H\alpha$	0·154	0·123	0·140
$H\beta$	0·085	0·070	0·070
$H\gamma$	0·062	0·057	0·057
$H\delta$	0·049	0·048	0·057

The results of the measurements are recorded in Table II. In this Table "1" and "2" denotes the ordinary doublet separation, as observed by us, "1" being the longer wave-length member and "2" the shorter one. The designation "3" denotes the third member of the triplet. Under the heading "2" and "3," it is assumed that "3" is shorter in wave-length than "2," while under the heading "3" and "1" we have taken "3" to be longer than the wave-length "1."

If the third members of the triplets had their origin in the spectrum of nitrogen the measurements recorded in Table II would indicate that in the spectrum of this element there should be wave-lengths either at $\lambda = 6563{\cdot}18$ Å.U. or $6562{\cdot}89$ Å.U., $\lambda = 4861{\cdot}56$ Å.U. or $4861{\cdot}41$ Å.U., $\lambda\, 4340{\cdot}72$ Å.U. or $4340{\cdot}54$ Å.U., $\lambda = 4101{\cdot}91$ Å.U. or $4101{\cdot}8$ Å.U.

In this connection it is interesting to note that, in the list of wave-lengths given for the spectrum of nitrogen by Kayser and Runge, wave-lengths are included at $\lambda = 4861{\cdot}4$ Å.U., $\lambda = 4342{\cdot}0$ Å.U. and $\lambda = 4101{\cdot}0$ Å.U.

As the secondary spectrum of hydrogen also includes wave-lengths at $\lambda = 4860{\cdot}28$ Å.U., and $\lambda = 4342{\cdot}07$ Å.U., the appearance of the triplet structure when the impure hydrogen was used, and its absence when the discharge was in the purified gas, is not altogether clear.

(5) *Summary of Results.*

(*a*) The following doublet separations were found for the first four members of the Balmer series $H_\alpha = 0{\cdot}154$ Å.U., $H_\beta = 0{\cdot}085$ Å.U., $H_\gamma = 0{\cdot}062$ Å.U. and $H_\delta = 0{\cdot}049$ Å.U.

When these separations were plotted against the squares of the corresponding wave-lengths they were shown to lie on a curve which pointed to the vanishing of the doublet separation at the short wave-length limit of the Balmer series.

(*b*) The wave-lengths H_α, H_β, H_γ and H_δ have been shown to consist of triplets when the electric discharge takes place in hydrogen containing a trace of nitrogen.

(*c*) Experiments made to decide whether the third members of the triplets had their origin in the radiations emitted by nitrogen atoms or in a modification produced by the nitrogen in the radiations emitted by the atoms of hydrogen were not decisive.

A Problem in the Theory of Heat Conduction.

By J. W. Nicholson, F.R.S.

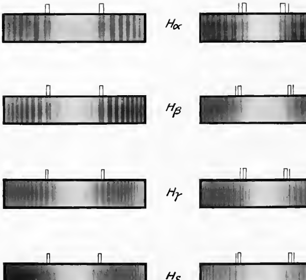
(Received September 29, 1921.)

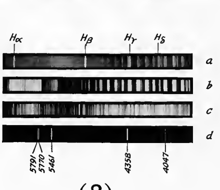
The first problem discussed in this paper is as follows :—" A long hollow cylinder is immersed in a medium of uniform temperature, and at a certain instant, is brought suddenly to a temperature above that of the medium, for example, by the passage through it of a stream of heated liquid. It is *maintained* at that temperature, and the temperature distribution in the outside medium at any instant, and the rate of leakage of heat from the cylinder, are required."

The main difficulty arises from the fact that the law of temperature on the surface of separation is arbitrary—we shall suppose, in the first instance, that it is constant. Solutions for the external temperature distribution are apparently known only when the surface has a given *initial* distribution, which is left to adjust itself without further direct supply of heat.

A solution for the distribution inside a cylinder whose surface is kept at zero temperature, and whose interior has any initial distribution, has been known for some time, and may be obtained by several methods. Perhaps

(1) (2)


H_α
H_β
H_γ
H_δ


H_α
H_β
H_γ
H_δ
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5791
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(3)